

Novel Microporous Molecular Frameworks: Potential for Gas Storage, Separation, and Catalysis

Scientific Achievement

Metal-organic framework solids are composed of infinite networks of transition metal ions connected to each other by organic linker molecules. Additional molecular species may be present to balance charge and, at least initially, to fill voids. Well established rules of coordination chemistry combined with the geometry of the linker molecules dictate the local topology of the framework; however, only exploratory research can reveal which of several possible overall structures are achieved. Within these constraints, the architecture of these networks may be finely tuned in order to achieve desired functionality.

The aminotriazole (AmTAZ) linker molecule is capable of binding to three transition metals in a dissymmetric fashion such that two metals are in close proximity, whereas the third is on the opposite side of the ligand. In a newly discovered series of ternary zinc-AmTAZ-anion salts, we have determined that AmTAZ greatly promotes the formation of microporous framework structures, due to its unique coordination geometry which favors curved internal surface fragments. The crystal structure adopted by these salts depends critically on the nature of the extra anion (required for charge neutrality). In the salts with chalcogenide anions, oxo- or sulfido-centered zinc clusters form the vertices of cages inside the framework. Each cage is large enough to accommodate approximately six H_2 molecules as guests. At least in the case of the sulfido salt, the gaps in the cage wall are sufficiently large to let small guest molecules pass through. The ternary salt with carbonate anion contains a highly complex, triply interpenetrating network of three-dimensionally connected channel systems with an average open pore diameter of more than 4 Å.

Significance

The work on the AmTAZ cage structures represents an initial success in the creation of porous networks for future use in gas storage. It demonstrates that dicarboxylate linkers (popular with many other researchers in this field) are not a required ingredient for the formation of robust framework solids. Of the three salts presented here, the carbonate-containing compound is the most intriguing due to its branched channel segments. Strategically located constrictions in the channels make this salt an excellent candidate for a gas separation system based on the size-selected kinetic drift velocity of the gas molecules, while the three-dimensional nature of the channel network prevents the clogging of the channels, as might be the case in systems with linear pores. Furthermore, the local pH distribution of the internal surfaces and the potential for the substitution of the zinc ions with redox-active transition metals holds promise for novel catalysis cycles. We envision the expansion of the pore networks in these framework materials by the incorporation of more extended AmTAZ analogs, such as bis(imidazolo)benzene fused-ring systems. Such larger pore systems may be capable of having their internal surfaces modified further (e.g. for specific catalytic applications) with the use of monolayer coating methods, such as atomic layer deposition (ALD).

Performers

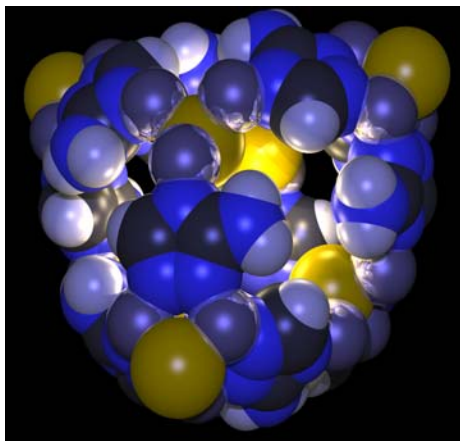
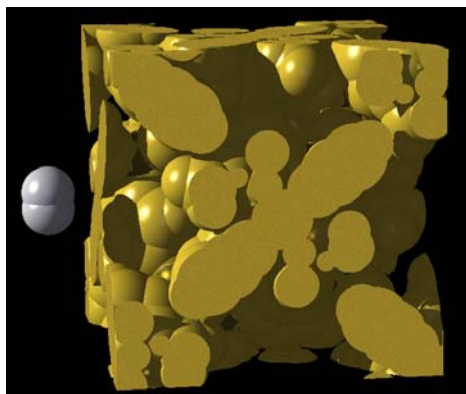
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Zn–AmTAZ–Anion Frameworks

Oxo Salt:

Void representation and H₂ molecule for comparison

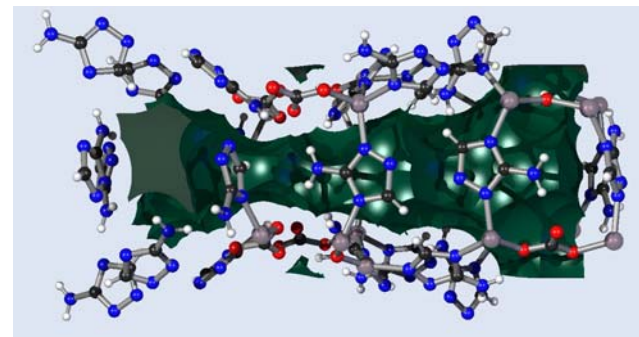


Sulfido Salt:

Cage representation

Gaps in cage wall are large enough to allow guest mobility

Carbonate Salt:



Ball&stick representation with pore volume (above); schematic representation of triply interpenetrated pore structure (below)

